

Stereoselectivity of the Oxymercuration of Cycloalk-2-en-1-ols. A Convenient Method for the Stereospecific Synthesis of *trans*-1,3-Diols

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THE addition of mercuric acetate to olefins has been demonstrated in most cases[†] to proceed in a *trans* manner.¹ The reaction, when carried out in an aqueous tetrahydrofuran solvent system, provides a highly stereospecific method for Markovnikov hydration.²

Henbest and Nicholls³ demonstrated the directive effect of the hydroxyl group upon the addition of mercuric acetate to cyclohex-3-en-1-ol. This work suggested the existence of an initial coordination of the mercuric moiety with the

hydroxyl group before attack on the double bond is effected. If such a premise is correct, the addition of mercuric acetate to cycloalk-2-en-1-ols should provide *trans*-1,3-diols.

We now report that the oxymercuration-demercuration of cyclohex-2-en-1-ol, cyclohept-2-en-1-ol, and cyclo-oct-2-en-1-ol proceeds preferentially to the *trans*-1,3-diols. The procedure used follows that described by Brown,² and differs only in the method of recovery of the product.[‡] After demercuration, the solution is neutralized by the

[†] Hindered olefins, such as norbornene and its derivatives, add mercuric acetate in a *cis*-manner.

[‡] The cyclo-octanediol was extracted with ether from the reduced solution after saturation with sodium chloride was effected.

cautious addition of 3M-HCl. The water-tetrahydrofuran mixture is decanted from the mercury and added to benzene. The benzene-water-tetrahydrofuran mixture is heated under reflux and the water is collected with a Dean-Stark trap. The benzene solution is evaporated to dryness under reduced pressure leaving a solid mixture of product and inorganic salts. The product is extracted with hot acetone.

The recovery of elemental mercury is quantitative. The absence of starting material from the tetrahydrofuran layer after demercuration indicates that the reaction is essentially complete. Yields and time of reaction are listed in the Table.

The apparent anomaly of the oxymercuration-demercuration of cyclohept-2-en-1-ol is also reflected in the epoxidation of cyclohept-2-en-1-ol.⁵ Whereas the epoxidation of cyclohex-2-en-1-ol and cyclooct-2-en-1-ol proceeds stereoselectively to the *cis*-⁶ and *trans*-epoxides⁴ respectively, the epoxidation of cyclohept-2-en-1-ol is reported by Cope to yield a mixture of the *cis*- and *trans*-epoxides in a 2:1 ratio.

Prior to this procedure for the preparation of *trans*-1,3-diols, the methods employed provided poor yields and substantial amounts of isomeric impurities.

The preparation and isolation of *trans*-cyclohexane-1,3-diol, as described by Rigby,⁶ from the hydrogenation of resorcinol, yields the diol in 38% after 60 crystallizations. The preparation of *trans*-cyclo-octane-1,3-diol is reported by Cope⁴ from cyclo-oct-2-en-1-ol in 42% yield and the product is contaminated with 29.4% of the isomeric *trans*-1,2-diol. *trans*-Cycloheptane-1,3-diol⁵

TABLE

Results realized for the preparation of *trans*-1,3-diols by the oxymercuration-demercuration of cycloalk-2-en-1-ols

	Yield (%)	Reaction time	
		<i>t</i> ^a	<i>t</i> ^b
Cyclohex-2-en-1-ol	50 ^c	10 sec.	2 hr.
Cyclohept-2-en-1-ol	65 ^d	20 sec.	10 hr.
Cyclo-oct-2-en-1-ol	70 ^e	2 hr.	18 hr.

^a Time for the yellow colour to disappear.

^b Recommended time for the reaction.

^c The product was homogeneous. Mixtures of the *cis*- and *trans*-1,3- and -1,2-diols were distinguishable on silicone oil at 110°. The product was shown to be free of three of the isomers, and when treated with acetic anhydride and pyridine was isolated as the diacetate, which had an i.r. spectra identical to an authentic sample of *trans*-cyclohexane-1,3-diol diacetate.

^d The product was converted to the diacetate. V.p.c. analysis indicated that the *trans*-1,3-diol (71%), *cis*-1,3- (27%) and -1,2-diol (2%) were present. Product yield was determined by comparison with an internal standard.

^e The product was recovered from ether upon concentration of the solution. The solid was recrystallized (benzene), m.p. 103—106°. Cope, *et al.*,⁴ recorded the melting point of *trans*-cyclo-octane-1,3-diol as 106.5—108°, and the corresponding diols as *cis*-1,2-(77.5—79°), *trans*-1,2-(31.0—32.5°), *cis*-1,3-diol (57.0—58.0°).

is formed in less than 25% yield and is accompanied by all three isomers. The utilization of the oxymercuration-demercuration reaction provides a convenient method for preparation of *trans*-1,3-diols in higher yield and far greater isomeric purity than previously recorded.

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⁵ A. C. Cope, Theodor A. Liss, and Geoffrey W. Wood, *J. Amer. Chem. Soc.*, 1957, **79**, 6287.

⁶ W. Rigby, *J. Chem. Soc.*, 1949, 1586.